Field Testing of an FGD Additive for Enhanced Mercury Control

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NETL Project DE-FC26-04NT42309
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Project Overview

- Field tests (pilot to full scale) of Degussa's TMT-15 additive for optimizing Hg capture by wet FGD
  - Prevent re-emissions
  - Minimize Hg in gypsum byproduct
- Co-funded by EPRI, TXU, Southern Company
- Test sites:
  - TXU Monticello (pilot wet FGD)
  - AEP Conesville (has dropped out due to recent OH results showing no re-emissions from Mg-lime FGD)
  - Southern Co. Plant Yates (pilot and full-scale JBR tests)

Degussa TMT-15

- 15 wt% aqueous solution of trimercapto-s-triazine, tri-sodium salt ($C_3N_3S_3Na_3$)
- Primarily used to precipitate divalent heavy metals from wastewaters

$$3\ Hg^{+2} + 2\ TMTNa_3 \rightarrow Hg_3TMT_2 + 6\ Na^+$$

- Currently used in 100’s of incineration plants worldwide to precipitate Hg before re-emissions reactions can occur in wet scrubbers

Hg-TMT Precipitates

- Divalent cation to trivalent anion precipitation leads to “cross linking”, produces precipitates large enough to filter, but much smaller than the bulk of the FGD solids
- Digestion of the Hg-TMT precipitate requires aqua regia under heat and pressure (i.e., more stable at low pH than other sulfides)
- Hg-TMT precipitates are thermally stable to 250^{o}C (480^{o}F)
  - Gypsum is calcined at 300^{o}F to make wallboard

TMT Properties

- Low toxicity to fish, water fleas, algae, etc.
- Mild irritant to skin, irritant to eyes
- No special PPE other than gloves, glasses or goggles with close-fitting side shields
- Not considered hazardous for transportation purposes

Potential Economics for Enhanced Hg Co-removal Using TMT-15

- TMT-15 costs about $4/kg as solution
- To prevent re-emissions:
  - Assume 20 $\mu g/Nm^3$ Hg in flue gas, 50% oxidized
  - Assume re-emissions at 2 $\mu g/Nm^3$ Hg
  - If TMT-15 is effective at 10x stoichiometric amount, cost is <$500/lb additional Hg removed
- To lower Hg content of gypsum (same assumptions as above):
  - Annual value of gypsum for 500-MW plant is $1.25 million ($5/ton)
  - Annual TMT-15 cost ~$30,000 or less

Testing Completed to Date

- First week of 2-week effort on Monticello pilot wet FGD conducted in April
  - Did not see any Hg re-emissions with Hg SCEM under baseline (no catalyst upstream, no TMT) conditions
  - Decided to instead focus on ability to produce low Hg content gypsum

Testing Completed to Date

- Delayed 2nd week of testing (week-long steady state test at optimum TMT dosage)
  - Since no re-emissions were seen (immediate SCEM feedback) needed to turn around analytical data on parametric test samples
  - Pilot wet FGD does not have primary dewatering
    - Need to add field separate gypsum from high Hg-content fines
    - New EPRI project is adding pump, hydrocyclones and tank to pilot wet FGD system for primary dewatering

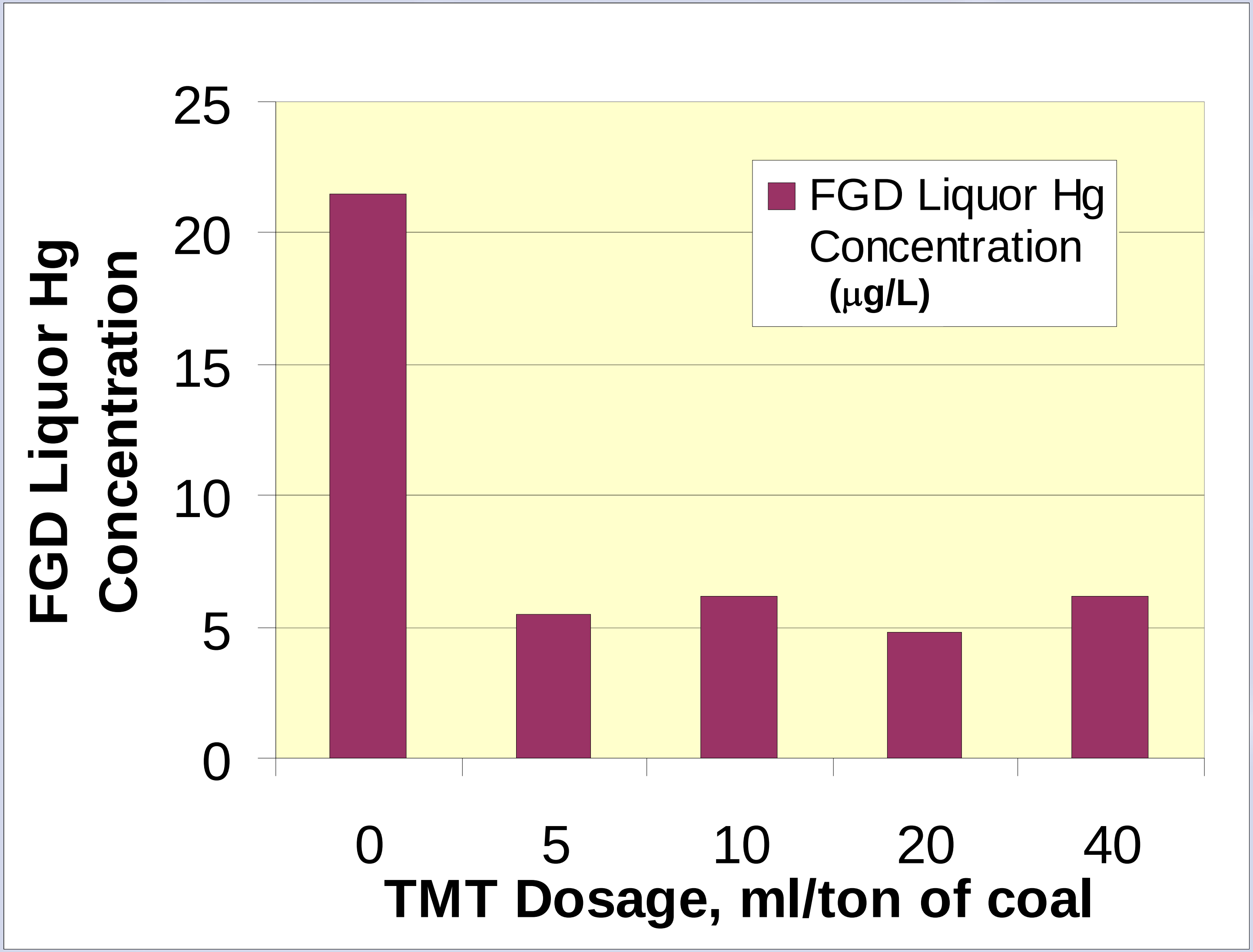
Interim Results of Parametric Tests at Monticello

- No apparent affect of additive on Hg removal across FGD
- Saw decrease in FGD liquor Hg conc. with TMT
  - No apparent TMT dosage effect
- Separated gypsum from fines in the laboratory by settling
  - Modest decrease in gypsum Hg conc. with TMT
  - No apparent TMT dosage effect
  - Effectiveness of TMT may be masked by contamination of gypsum with fines in settled samples
  - Need field dewatering to determine true ability to separate high-Hg salts from gypsum

FGD Pilot Unit at Monticello Station

TMT
Injection

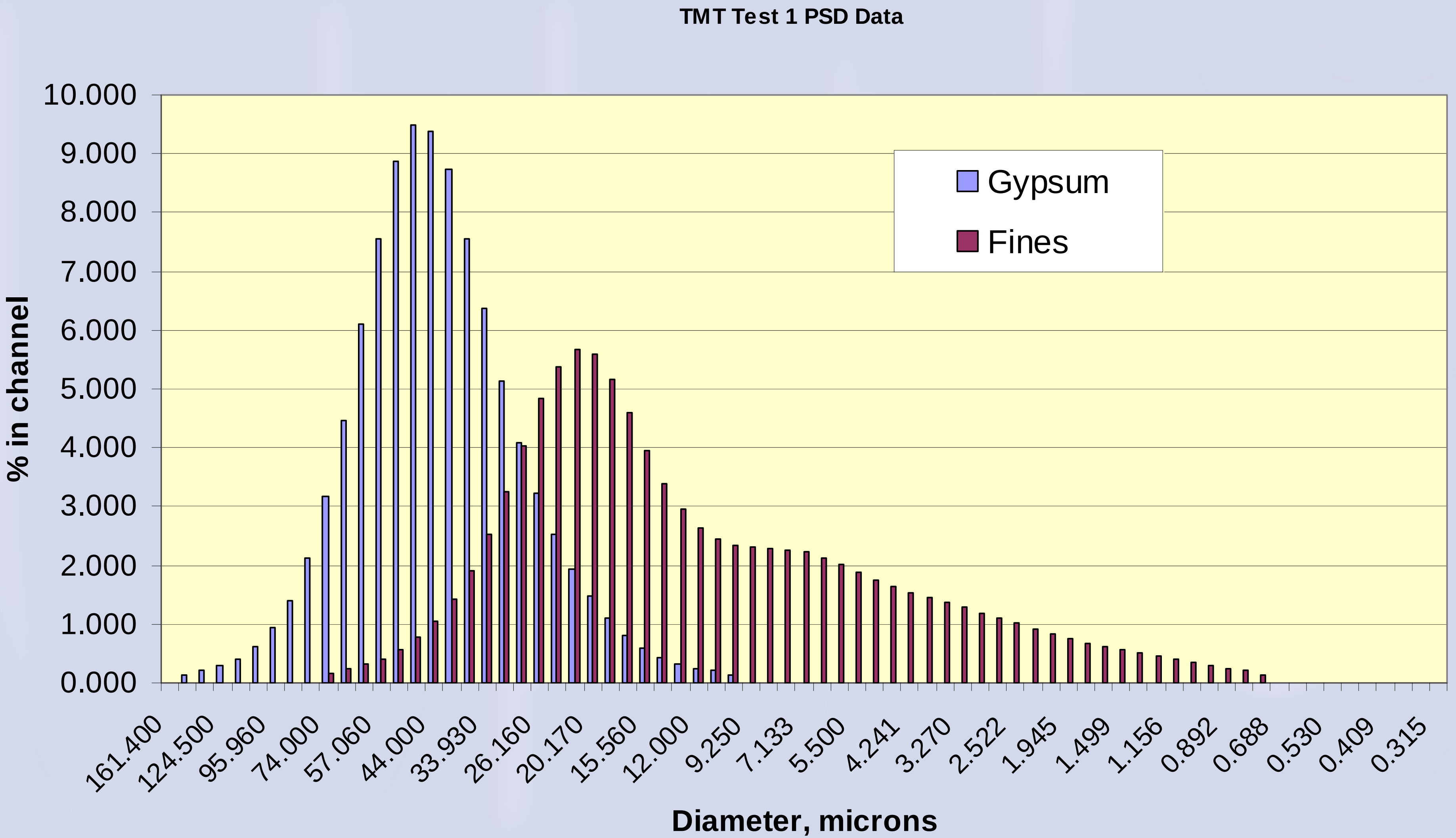
FGD Liquor Hg Concentrations



Settled FGD Solids Sample Hg Concentrations

TMT Dosage (ml/ton of coal)	Wt% gypsum phase in slurry	Gypsum Hg Content, μg/g (% of Hg in slurry)	Wt% fines in slurry	Fines Hg Content, μg/g (% of Hg in slurry)
0	11.6	1.7 (53%)	0.3	55 (44%)
5	9.2	1.2 (33%)	0.5	39 (65%)
10	10.7	1.2 (36%)	0.3	75 (62%)
20	10.0	1.0 (33%)	0.4	52 (63%)
40	9.3	1.2 (36%)	0.3	57 (61%)

Example PSD for Gypsum and Fines Phases (5 ml/ton TMT-15 dosage)



Future Testing Plans

- Will complete second week of tests at Monticello when dewatering equipment is ready
- Pilot JBR parametric tests planned for Plant Yates in early August
- Full-scale JBR steady state test planned for Plant Yates in the fall
- **Need replacement for AEP Conesville**
  - Desire a site with known, significant re-emissions levels
  - Mg-lime FGD with natural oxidation, no SCR in service?

Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors

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Introduction

- **Project Goal** – develop a fundamental understanding of Hg "re-emissions" from wet FGD systems
  - Seen as FGD outlet Hg^0 concentration > inlet Hg^0
  - Apparent reduction of Hg^{+2} removed in FGD absorber
  - Limits overall Hg removal by FGD system
- **Technical Approach** – conduct kinetics experiments, kinetics modeling, and bench-scale wet FGD model validation tests
- **Expected Benefits** – the ability to predict FGD re-emissions, and optimize FGD conditions to minimize or eliminate

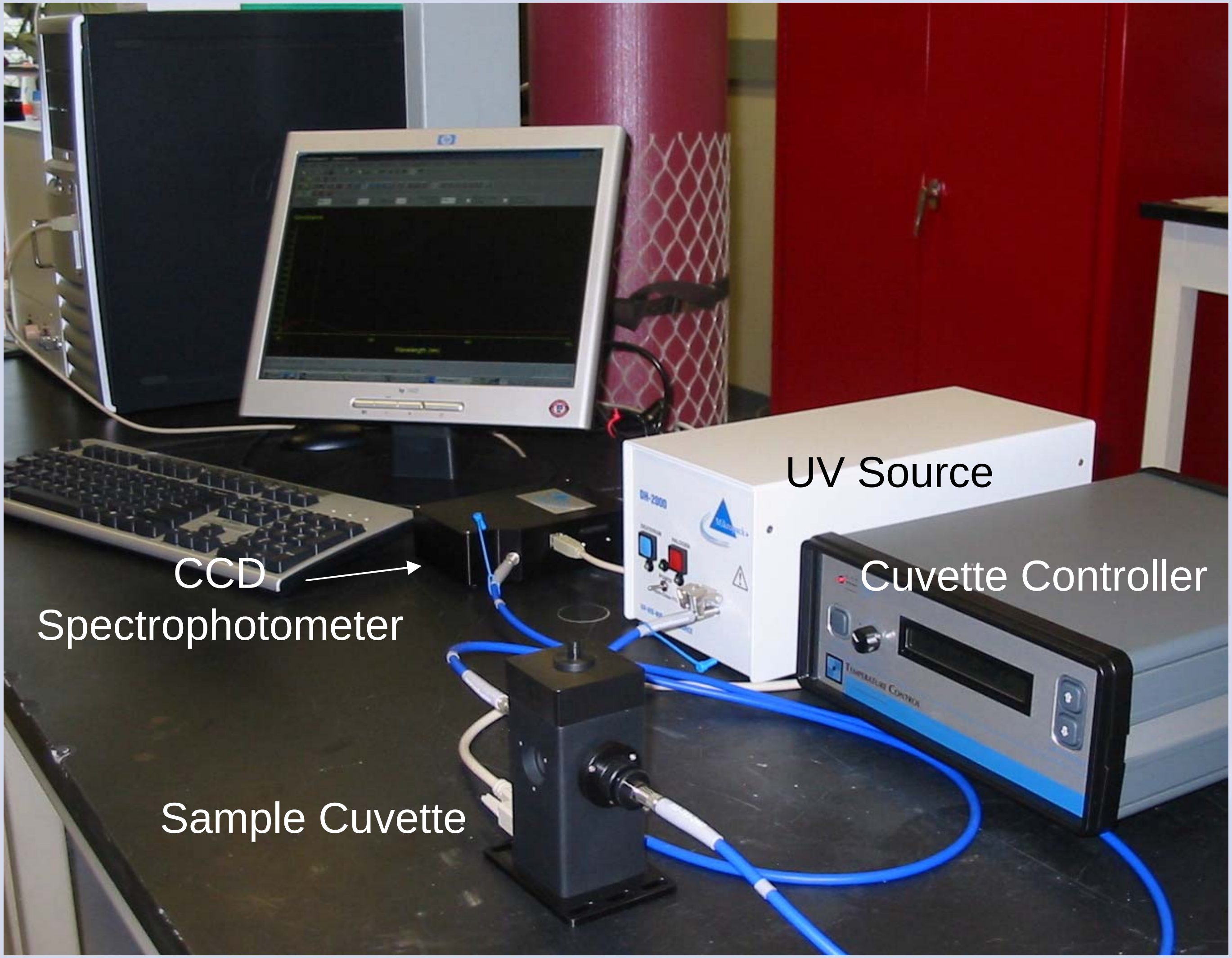
Main Project Elements

- Measure kinetics using both spectroscopy of the Hg^{2+}-Sulfite complex reactants, and production / stripping of Hg^{o}
- Extend reaction conditions to include presence of chloride, thiosulfate and additives, and into the FGD pH region
- Construct a kinetics model which describes the results
- Test the model using the URS bench scale FGD

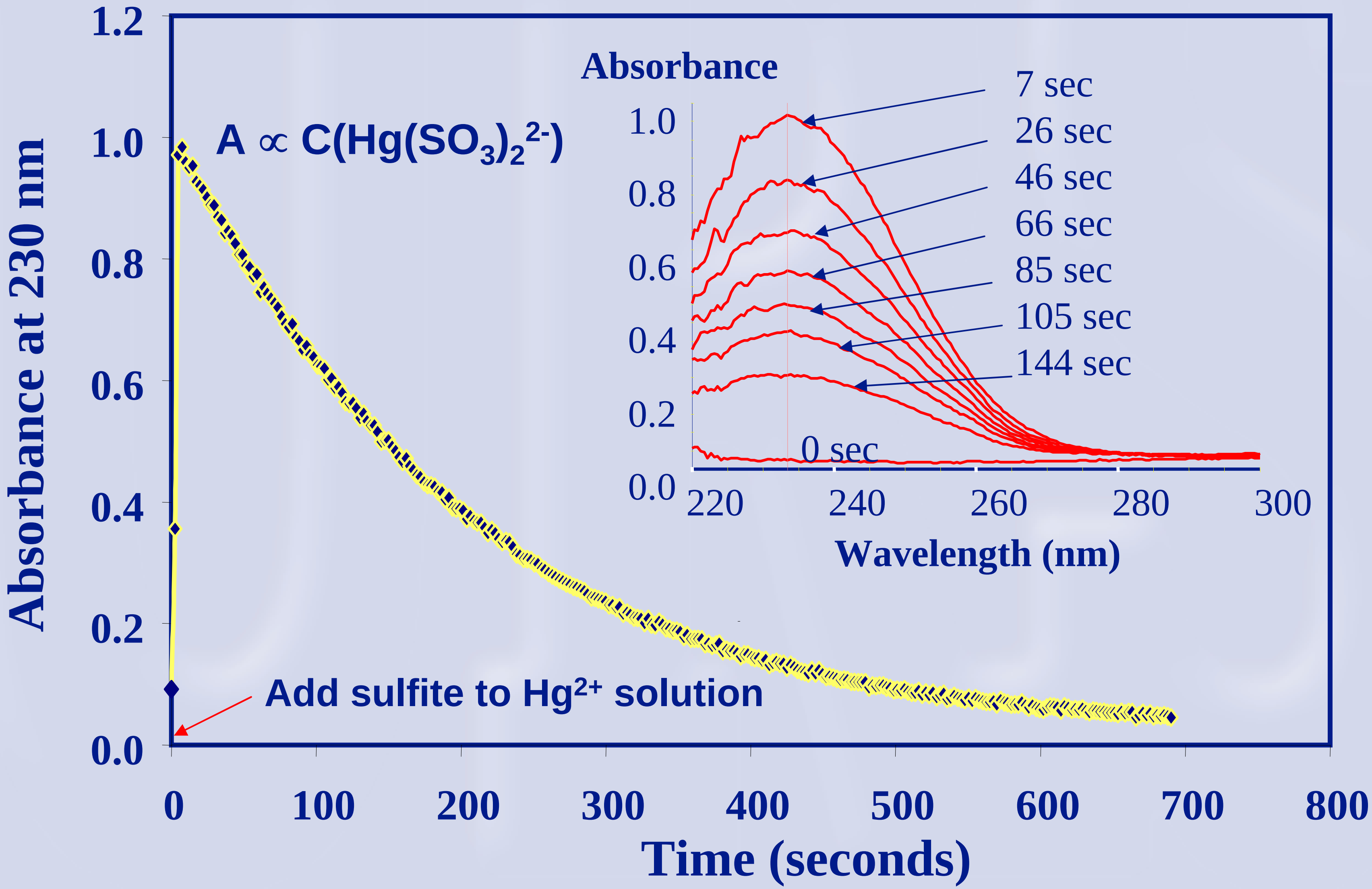
Main Chemical Reactions for Hg Emission without Chloride

- Overall reaction:
  - $Hg^{2+} + HSO_3^- + H_2O \rightarrow Hg^o\uparrow + SO_4^{2-} + 3\ H^+$
- Main pathway is through mercuric-sulfite complexes:
  - $Hg^{2+} + SO_3^{2-} \leftrightarrow HgSO_3$
  - $HgSO_3 + SO_3^{2-} \leftrightarrow Hg(SO_3)_2^{2-}$
- Equilibrium favors $Hg(SO_3)_2^{2-}$ in presence of excess sulfite
- But only $HgSO_3$ decomposes to give reduction of Hg^{2+}:
  - $HgSO_3 + H_2O \rightarrow Hg^o\uparrow + SO_4^{2-} + 2\ H^+$

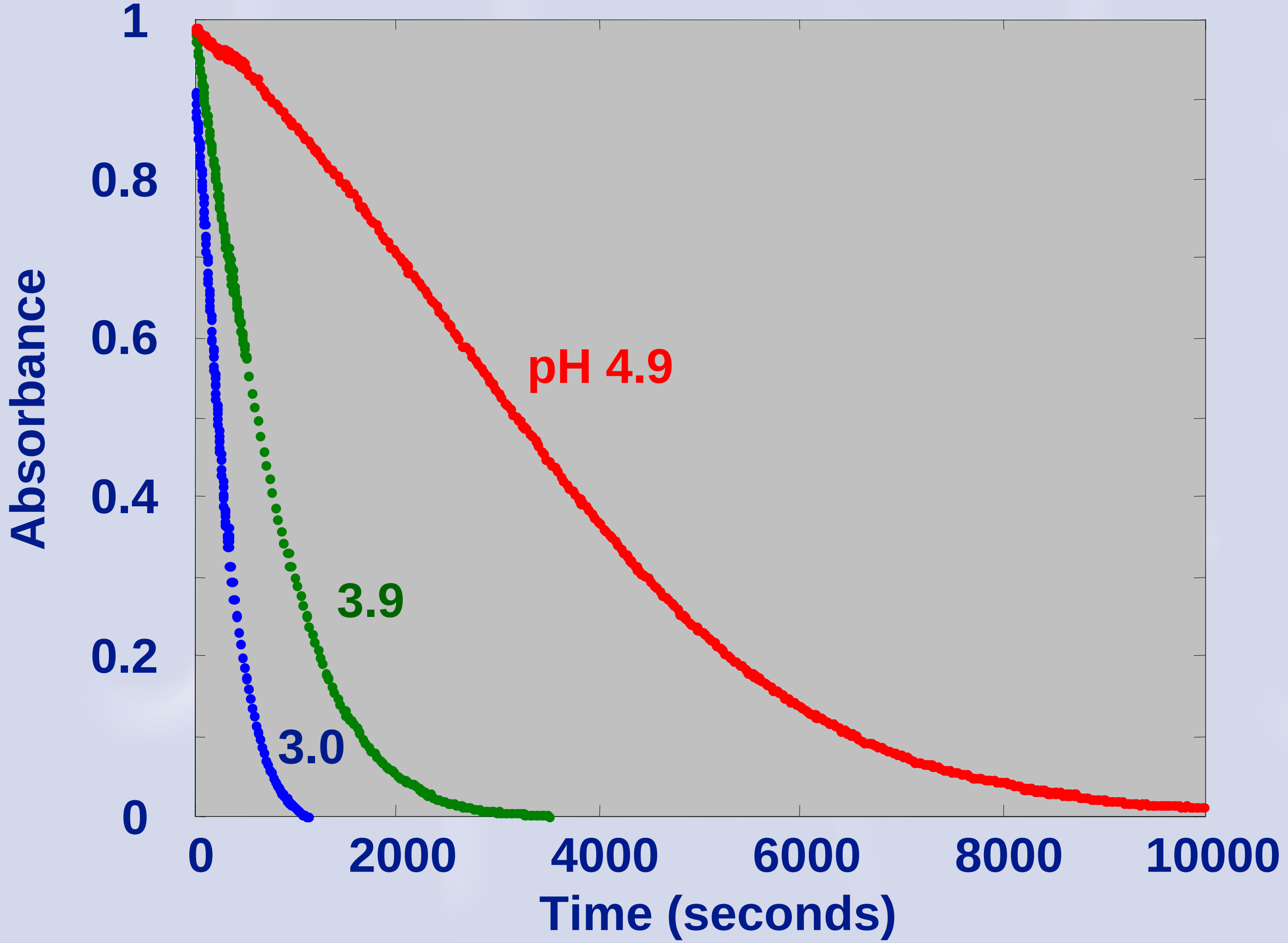
URS UV/Visible Spectrophotometer



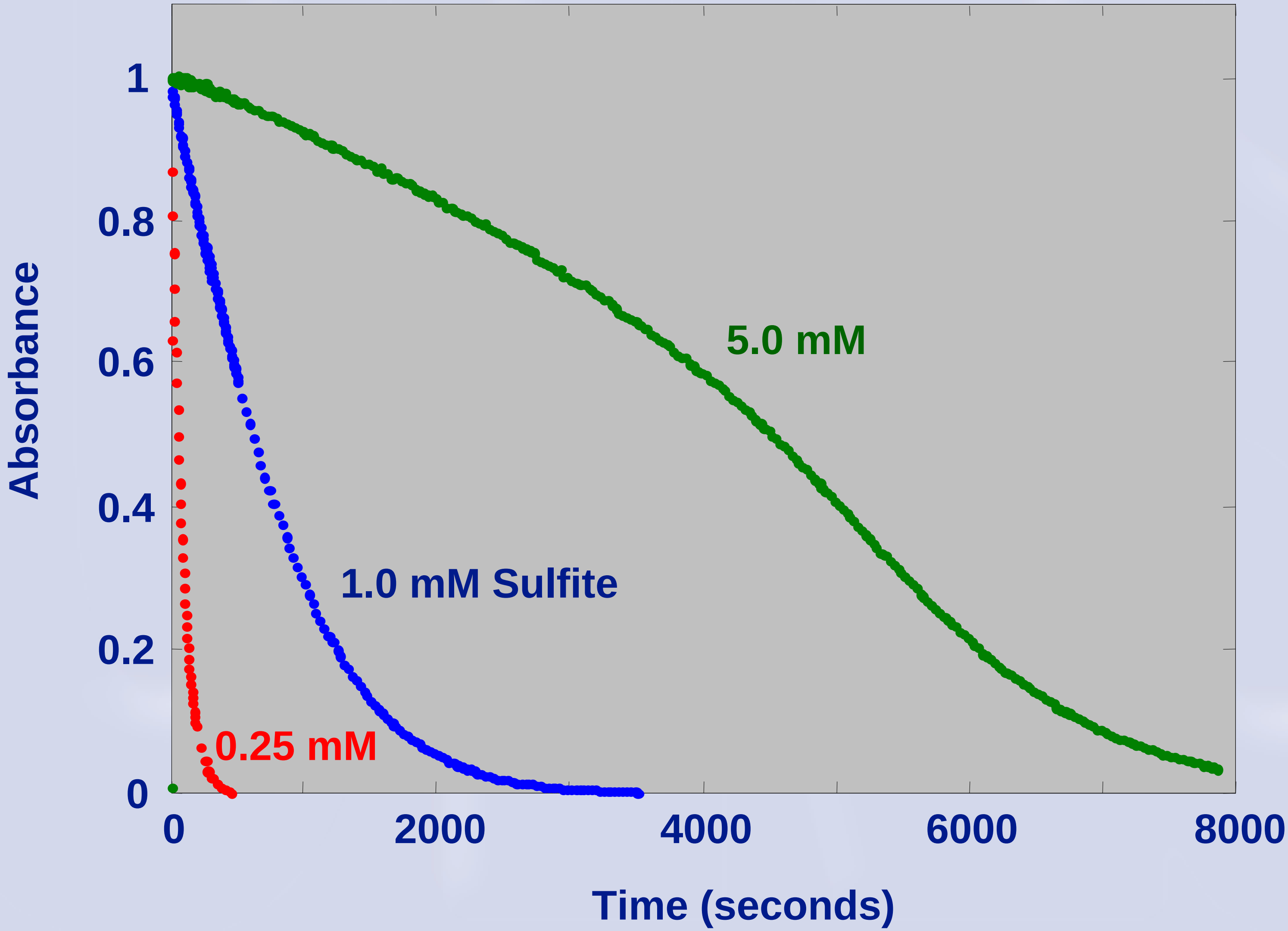
Example Spectra and Rate Curve



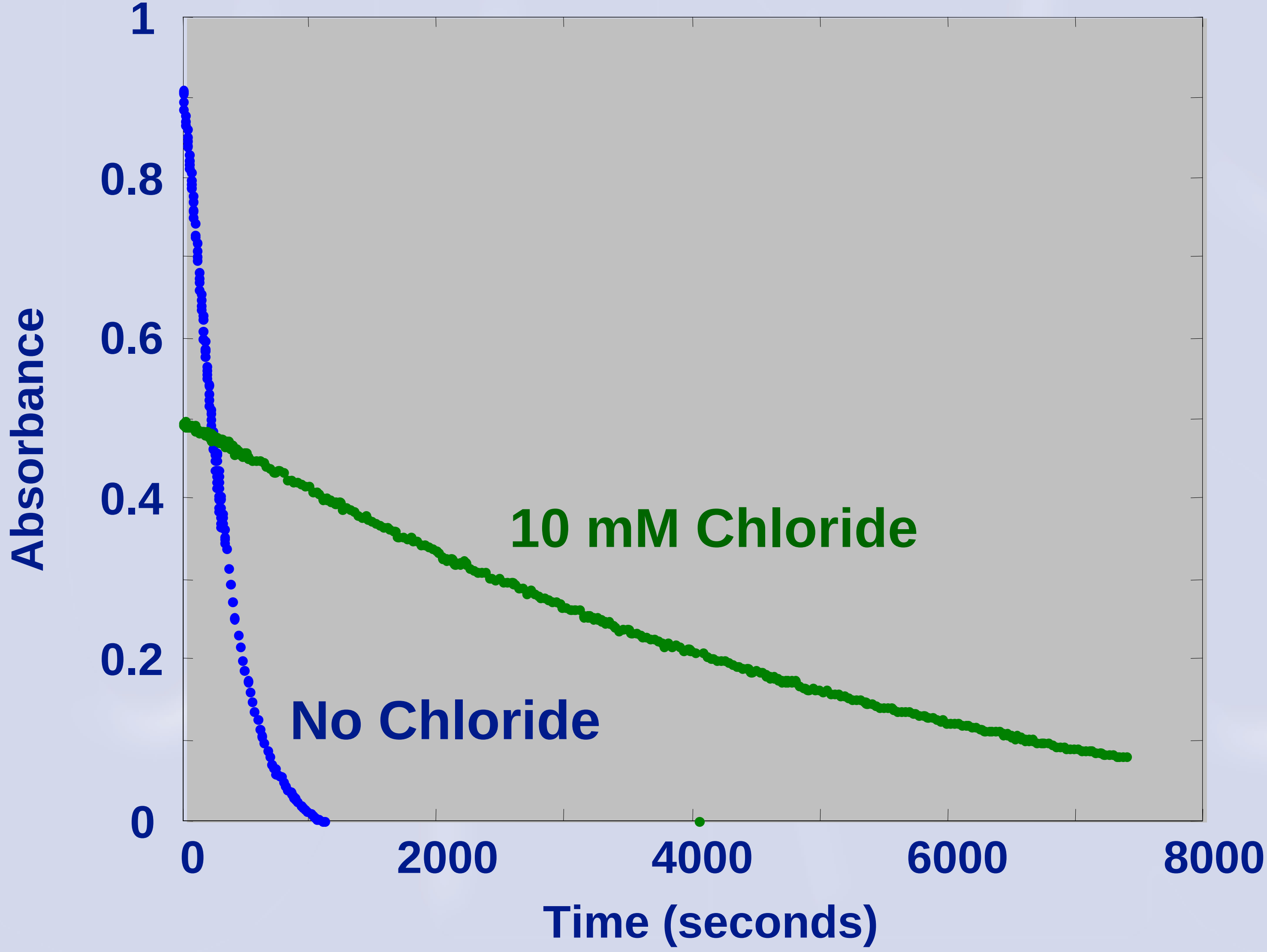
Effect of pH on Rate Curves without Chloride. 1.0 mM sulfite, 55º C, 40 microM Hg^{2+}



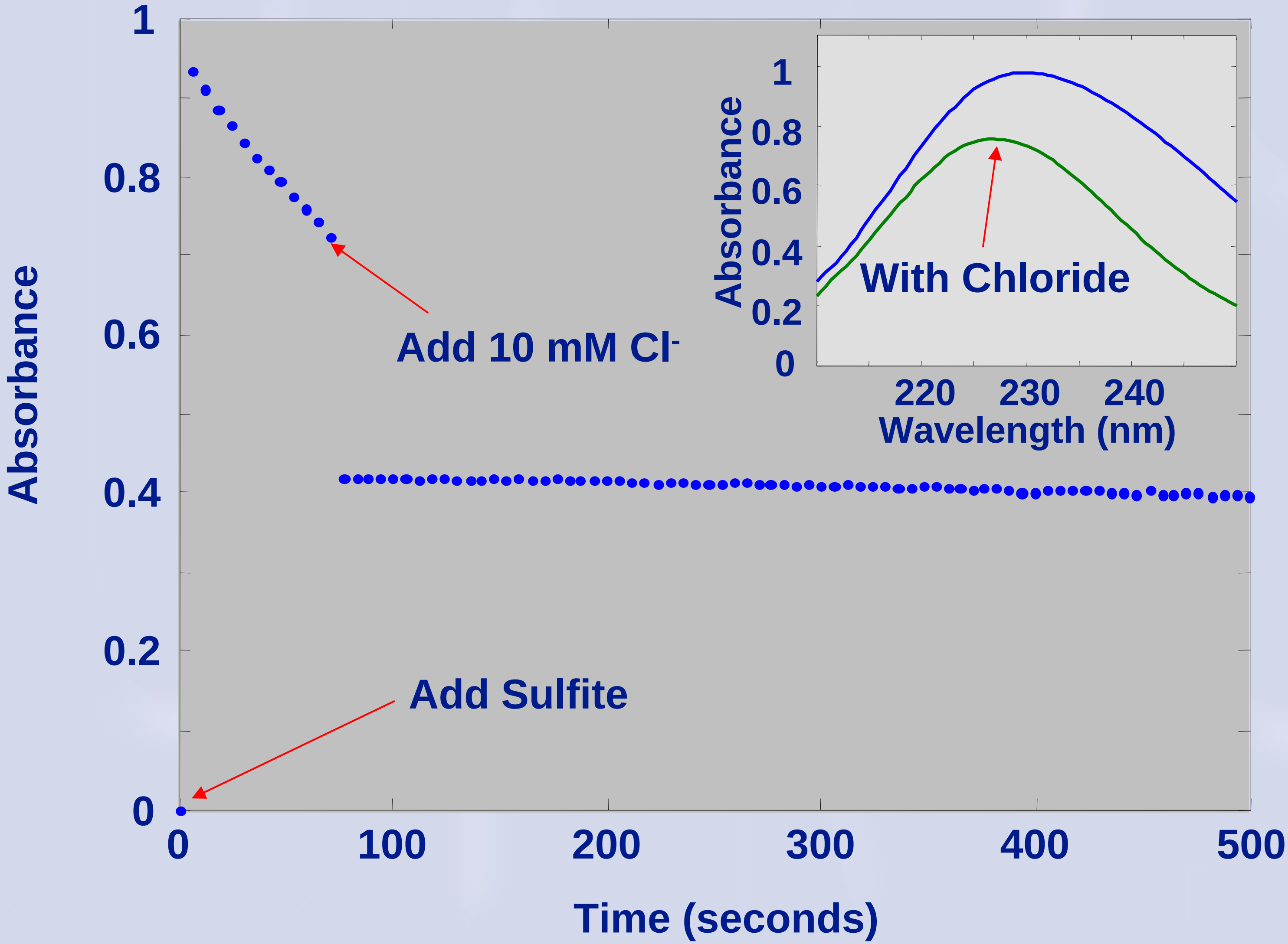
Effect of sulfite on rate curves without chloride; pH 3.9



Effect of Chloride on Rate Curve at pH 3.0 and 1.0 mM Sulfite



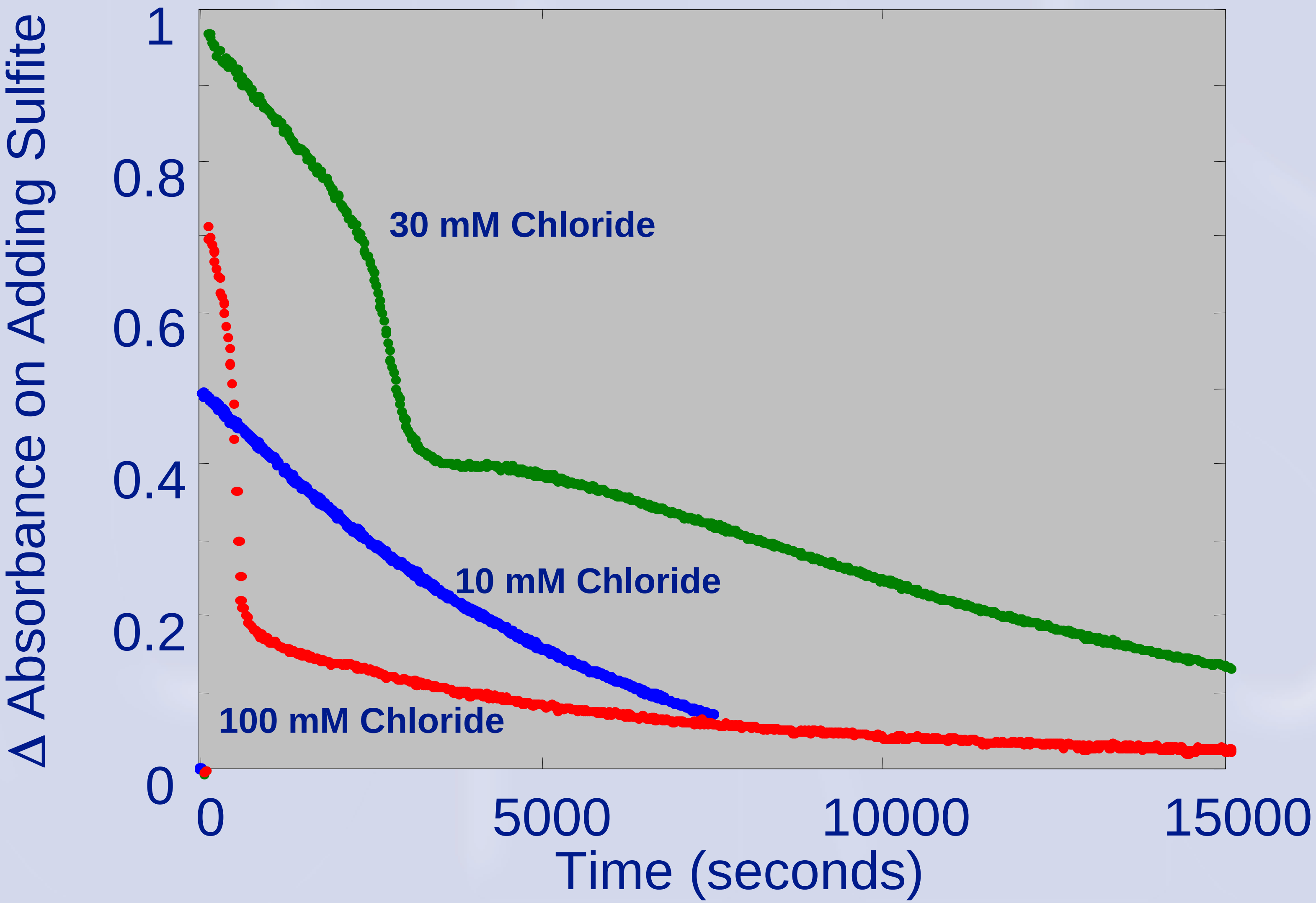
Adding chloride during the run; pH 3.0; 1.0 mM sulfite



Reaction Mechanism Observations

- Chloride evidently causes a change of mechanism - new intermediate, $ClHgSO_3^-$
- But also observe complex “composite” reaction behavior without chloride
- "Slow" reaction conditions tend to give complex response such as a large increase in reaction rate after an initial “induction time”
- Several factors affecting this behavior are under investigation

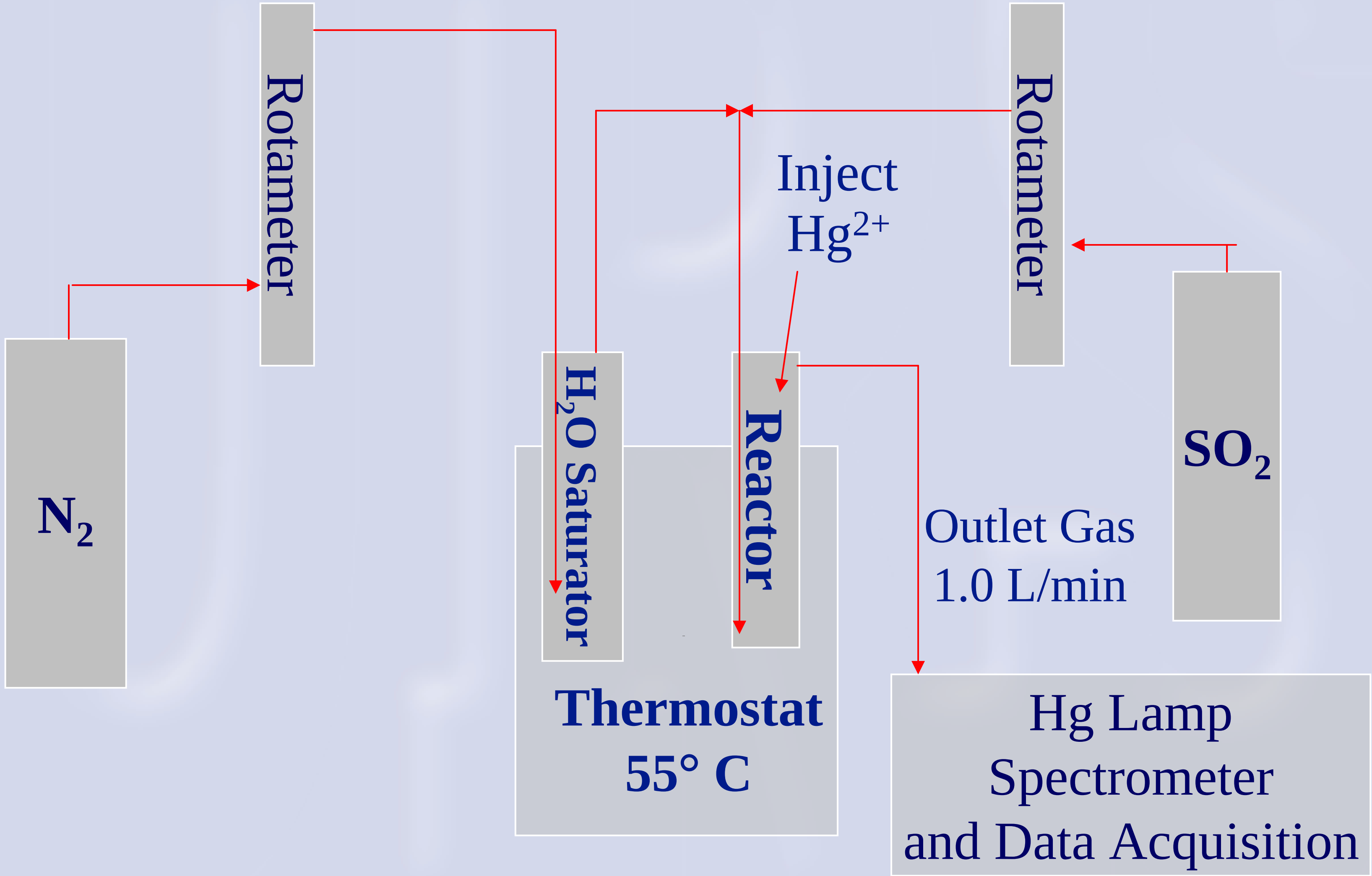
Induction Time Behavior in Chloride Solutions



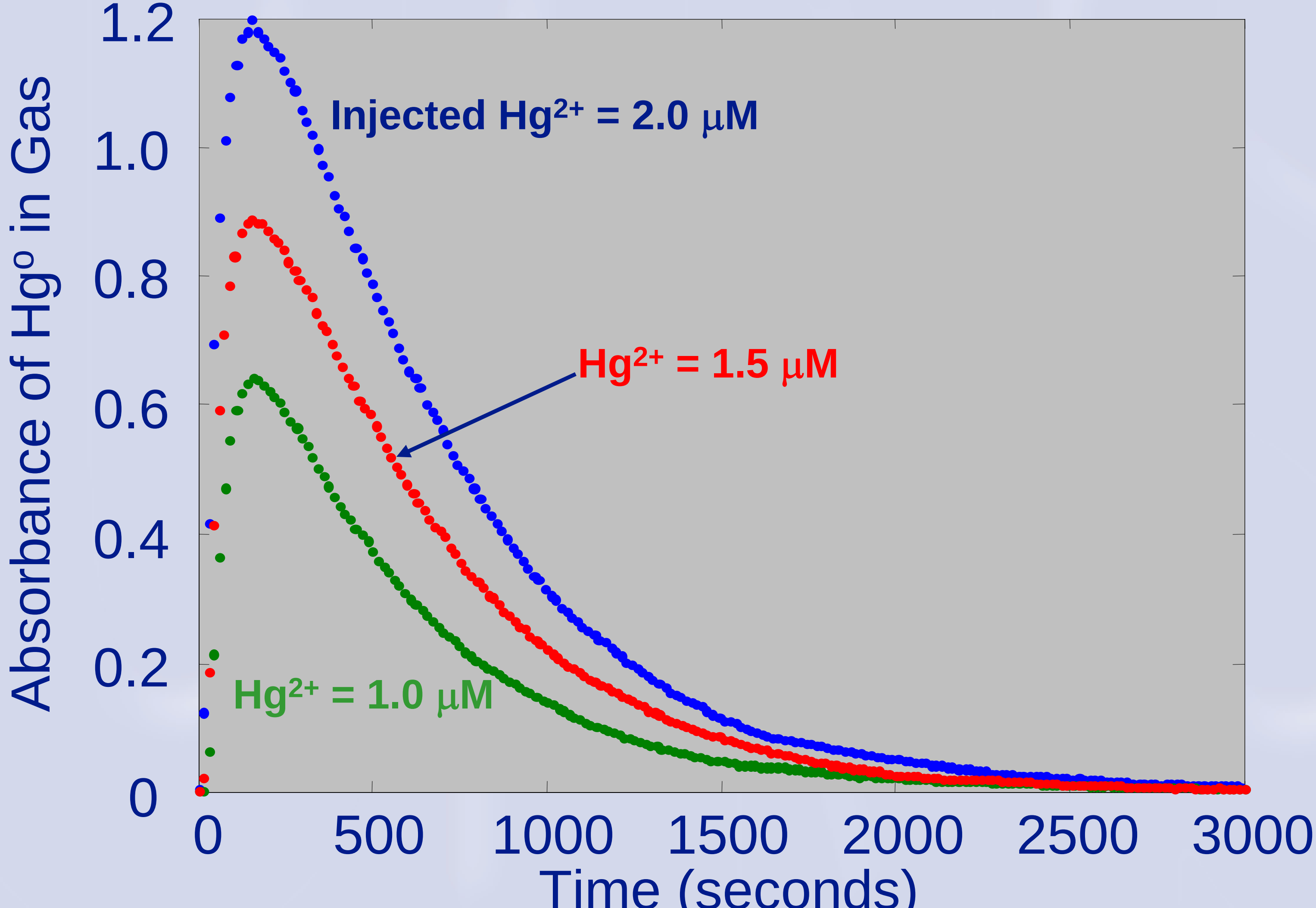
Stripping Method for Measuring Hg^0 Emissions from Test Solutions

- Continuously measures Hg^0 in gas phase as it is emitted following Hg^{+2} injection and stripping from reactor
- Able to use low “FGD levels” of Hg^{2+} in reactor: 0.5 – 2 micromolar
- Getting close material balances on Hg^{2+} added, Hg^0 measured in gas phase, and Hg left in liquid (which is usually negligible)
- Exponential decay rates are independent of initial Hg^{2+} concentration, matching spectroscopic results

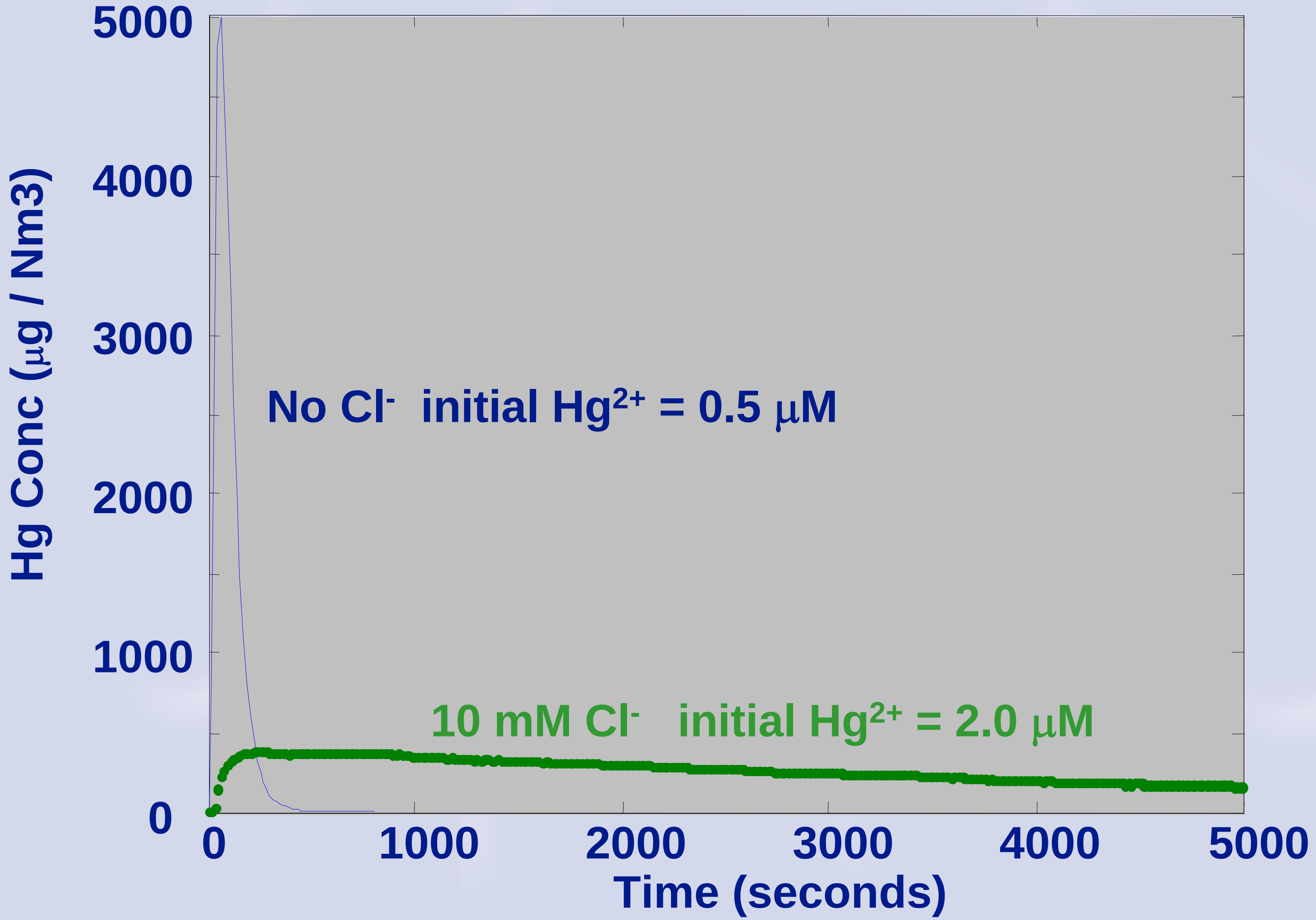
Hg^0 Stripping Kinetics Apparatus



Stripping Runs at Different Initial Hg^{2+} Concentrations



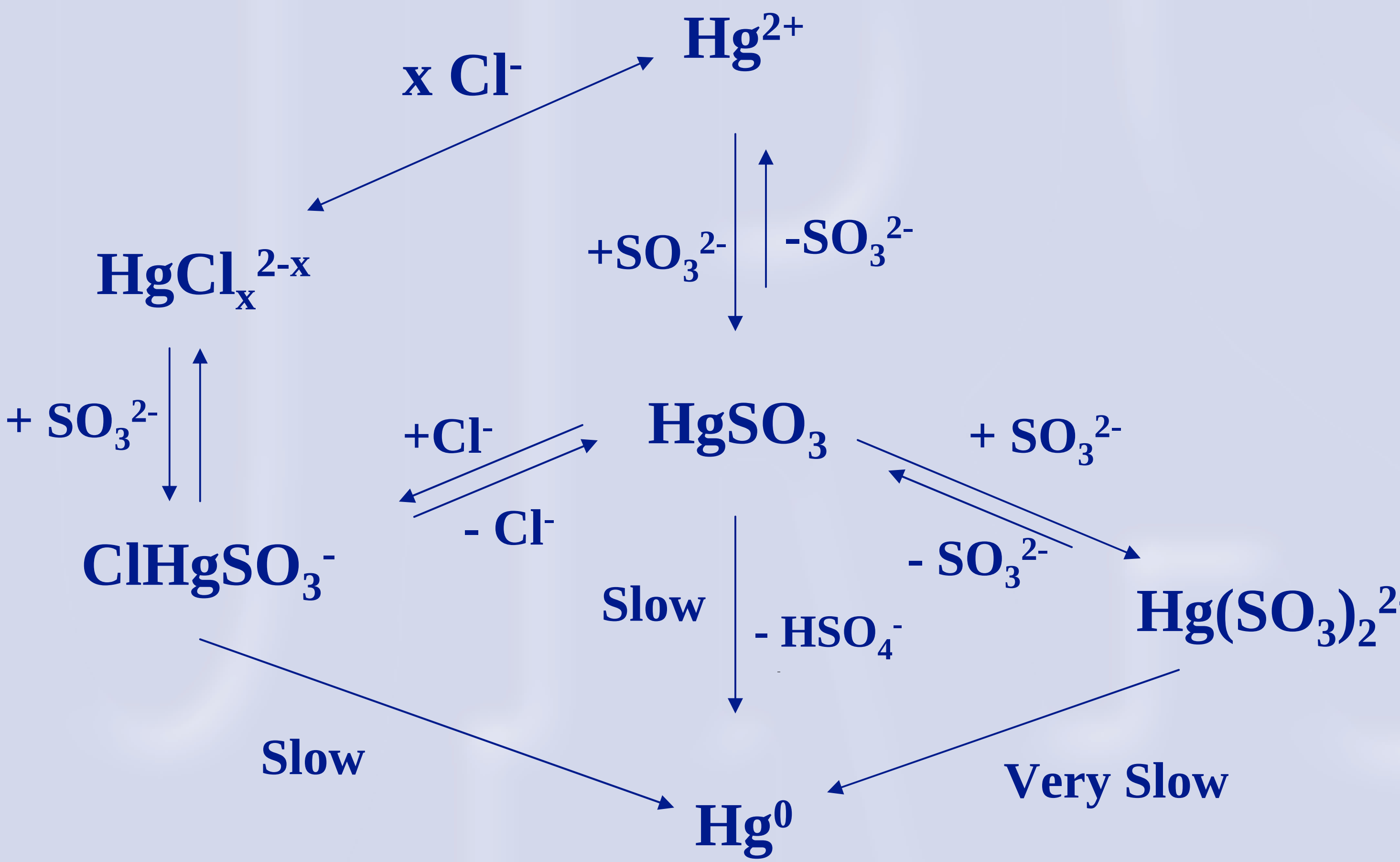
Effect of Chloride on Hg^0 Stripping Kinetics



Kinetics Modeling

- URS modeling software maintains database of reactions, rate constants, and reaction conditions - initial concentrations, pH, temperature
- Calculates concentration-time profiles for all chemical species and intermediates
- Develop model by comparing experimental and calculated results while varying rate parameters until results match experiment over a wide range of conditions

Major Reaction Pathways



Project Status and Conclusions

- Developed experimental methods for following reactants and products independently
- Determining effects of pH, sulfite, temperature, ionic strength, and other "FGD" components on reaction rates
- Chloride has major effects on reaction rates and mechanism
- New reaction intermediates proposed; in process of constructing model using these mechanisms